

DSC SENSITIVITY TO HYDRATED MINERALS IN PLANETARY SAMPLES

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Introduction. Differential scanning calorimetry (DSC) is well established as a method for determinative mineralogy [1] although its application to extraterrestrial materials has been limited [2]. In addition to laboratory usage, DSC has been proposed as an in-situ analyzer for planetary surface materials [3,4]. Here we assess the sensitivity of DSC for detection of hydrated minerals in planetary rock, soil, or regolith samples and, specifically, for basalt, which may be the most widespread rock clan on terrestrial-type planets [5].

Sensitivity and resolution of DSC data can be defined by analogy with spectroscopy (Fig. 1). For a given pure sample material, DSC sensitivity and resolution are affected by scan (heating or cooling) rate, gaseous purge rate, and composition of the purge gas. For mixed-phase materials, sensitivity and resolution are also affected by additivity of signals (including peak overlap) from two or more thermally active phases as well as from chemical reactions between phases. Empirical evaluation of sensitivity is essential for complex samples.

DSC sensing of water-bearing minerals is based upon enthalpic peaks produced by thermally stimulated dehydration. For a single transition, $\Delta H(x_i) = kX \Delta H(p_i)$, where $\Delta H(x_i)$ is the integrated dehydration peak for mineral i in the mixture, $\Delta H(p_i)$ denotes the corresponding peak measured for pure component i , and X is the mass fraction of i in the mixture. The proportionality is $k \leq 1$, with the precise value depending on the degree to which component i interacts with its host matrix.

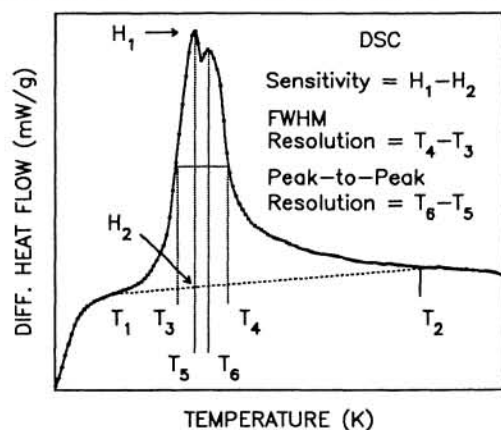


Figure 1. Sensitivity and resolution defined for DSC peaks.

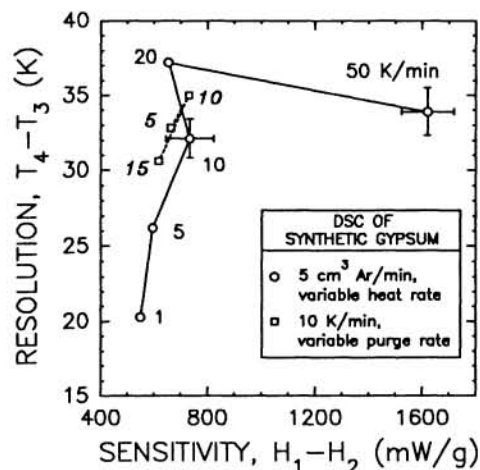


Figure 2. DSC sensitivity and resolution for pure synthetic gypsum.

Each error bar represents one standard deviation of the mean for replicate analyses.

Samples and Methods. Precisely weighed powders of individual hydrated minerals were blended in an agate ball mill with U. S. Geological Survey standard basalt BHVO-1 to yield a series of homogenized two-component mixtures. Such mineral/basalt mixtures were prepared for gypsum (synthetic), goethite (synthetic), hydromagnesite (synthetic), chabazite (Arizona, USA), clinoptilolite (Wyoming, USA), and nontronite (Germany; Clay Minerals Society NG-1). Individual samples of 10-20 mg were analyzed at 300-1000 K in a Perkin-Elmer DSC-2C instrument using unsealed aluminum oxide containers and a dynamic gaseous purge of high-purity argon. Unusually low purge rates (by laboratory standards) were used to simulate those that might be dictated in highly constrained planetary surface analyzers. Instrument calibrations were maintained by regularly melting standard zinc metal (National Institute of Standards and Technology SRM-2221) and indium metal (NIST GM-758).

Results. The instrumental response showed the expected inverse variation of resolution with sensitivity as a function of scan rate; the low purge rates had only a second-order effect (Fig. 2). As also expected, well-crystallized minerals with H₂O or OH⁻ in highly ordered structural sites gave sharp peaks whereas poorly crystallized minerals (or those with water in more poorly ordered sites) gave broad peaks. For the latter minerals (e.g., clinoptilolite, nontronite), peak recognition and integration by ordinary methods was highly

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uncertain for $X < 10$ wt. %. In contrast, the well-crystallized hydrates (gypsum, goethite, hydromagnesite) gave definitive peaks at $X \leq 1\%$. Chabazite gave much better results than clinoptilolite, possibly because the former contains more water per formula weight than the latter. For the well-crystallized hydrates, sensitivities as low as $X = 0.5\%$ are readily achievable at a modest scan rate (10 K/min) (Fig. 3). For all minerals that give intrinsically poor enthalpic peaks, detectability can be improved by more advanced data-analysis methods such as Fourier self-deconvolution (Fig. 4). For example, deconvolution analysis should improve sensitivity for nontronite to about $X = 3\%$ or better. Because increasing the heating rate from 10 K/min to 50 K/min produces a factor-of-two increase in sensitivity with only modest loss of resolution (Fig. 2), the detection limits depicted in Figs. 3 and 4 might be further improved at higher scan rates. Increasing the scan rate, however, has the additional complication of shifting peak temperatures upward. As a consequence for in-situ planetary applications, faster heating would require a higher temperature DSC furnace (hence, more electrical power) in order to fully integrate the shifted peaks.

At least in laboratory applications, with optimum scan rate and data deconvolution, ultimate detection limits for two-component mixtures might be 1-2% for nontronite and $\leq 0.2\%$ for hydrated salts.

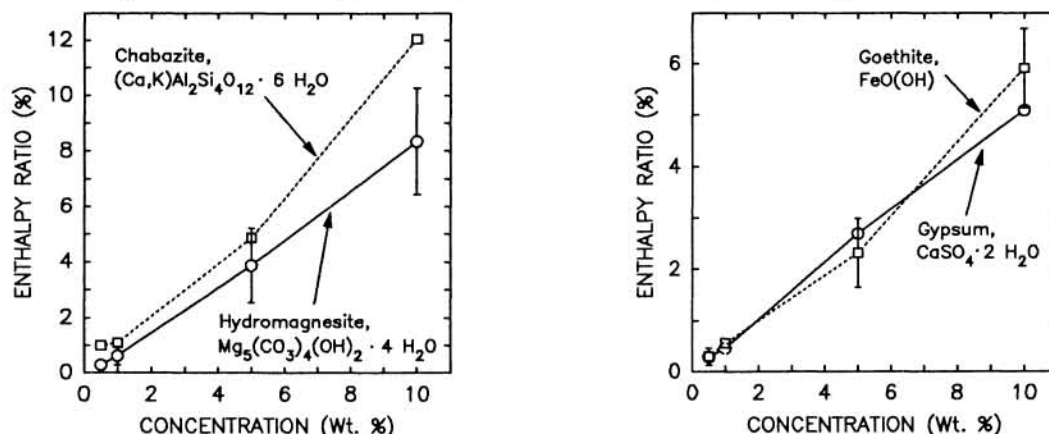


Figure 3. Enthalpy-ratio factors (10 K/min heating, $5 \text{ cm}^3 \text{ Ar/min}$), kX , as a function of mineral concentration in mineral/basalt mixtures. All four minerals are detectable at 0.5 % concentration. Each error bar denotes one standard deviation among three analyses; precisions are similar for all minerals but, for clarity, error bars are shown for only one series in each chart. Each mineral analysis is based on a single dehydration peak except for hydromagnesite which combines four decrepitation peaks.

Conclusions. Minor to trace concentrations of hydrated minerals can be detected in a basalt matrix by DSC. For smectite-type clay minerals, the detection limit is projected to be in the 1-10 wt. % range but for well-crystallized hydrated oxides, carbonates, and sulfates the limit is probably ≤ 0.5 wt. %.

References:

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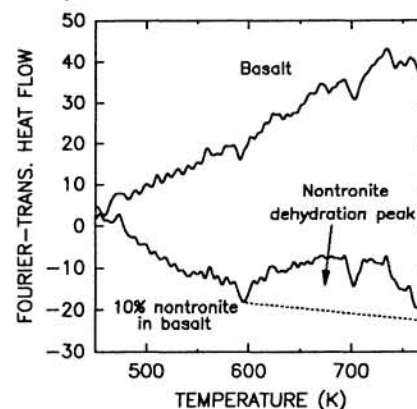


Figure 4. DSC peak enhancement through Fourier self-deconvolution (Bessel function, $\gamma = 0.05$, filter = 1) by the method of [6].